Chlorine Abundances In Martian Meteorites. D. D. Bogard¹, D. H. Garrison², and J. Park³. 1-Code KR, NASA-JSC, Houston, TX 55058 (donald.d.bogard@nasa.gov). 2- Barrios Technology JE23, 2224 Bay Area Blvd., Houston, TX 77058. 3-NASA-MSFC, Huntsville, AL.

Chlorine measurements made in martian surface rocks by robotic spacecraft typically give Cl abundances of ~ 0.1 -0.8% (1, 2). The average Mars global surface abundance of Cl measured from orbit is estimated at 0.48% (3). In martian rocks, Cl correlates with S, and both likely were concentrated on the martian surface by volcanic emissions and in martian rocks by near-surface water interactions (1,2,4). In contrast, Cl abundances in martian meteorites appear lower, although literature data are limited, and martian nakhlites were also subjected to Cl contamination by Mars surface brines. Chlorine abundances reported by one lab for whole rock (WR) samples of Shergotty, ALH77005, and EET79001 range 108-14 ppm, whereas Cl in nakhlites range 73-1900 ppm (Table 1). Measurements of Cl in various martian weathering phases of nakhlites varied 0.04-4.7 percent and reveal significant concentration of Cl by martian brines (7).

At JSC we have performed Ar-Ar age dating of whole rock and separated mineral phases of several martian meteorites (e.g., 8,9). Neutron irradiation of these samples produce ³⁸Ar from ³⁷Cl. Although terrestrial atmospheric ³⁸Ar, trapped martian ³⁸Ar, and ³⁸Ar produced by cosmic ray interactions are also present in these samples, we previously showed how consideration of the Ar isotopic data as a function of stepwise temperature release of Ar can be used to identify these individual ³⁸Ar components (10). Briefly summarized, we adopt the ³⁶Ar/³⁷Ar ratio (³⁷Ar is produced in the reactor by neutron capture on Ca) measured in high-temperature Ca-rich phases as being a pure nuclear component, and subtract this ratio from measured ³⁶Ar/³⁷Ar at all extractions to give trapped (terrestrial and martian) ³⁶Ar. For each extraction, we then multiple ³⁶Ar_{cos} by 1.5 to obtain ³⁸Ar_{cos} and trapped ³⁶Ar by 0.188 to obtained trapped ³⁸Ar. Subtracting these ³⁸Ar components from measured ³⁸Ar gives excess ³⁸Ar produced from Cl (³⁸Ar_{Cl}) for each extraction. Because this technique permits determination of 38 Ar_{C1} with increasing temperature, and because all terrestrial and at least some martian Cl incorporated onto grain surfaces by weathering is expected to degas from the sample at lower extraction temperatures, this method permits, to some degree. separation of primary Cl indigeneous to the minerals from Cl on weathered grain surfaces. The uncertainty in these Cl abundance calculations are estimated at $\sim 10\%$ for measuring relative abundances of ³⁸Ar in the meteorite and the co-irradiated Cl standard, and about

8% for absolute Cl in the irradiation standard (10), or \sim 18% overall.

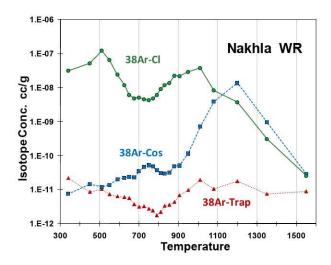
Figure 1 shows the result of using this technique to divide the temperature release of 38 Ar from Nakhla WR into three ³⁸Ar components – cosmogenic, trapped, and ³⁸Ar_{Cl}. Because 96% of the total ³⁸Ar was produced from Cl, subtraction of minor cosmogenic and trapped ³⁸Ar do not significantly affect the calculation. For Nakhla, ³⁸Ar_{Cl} is primarily released in two peaks centered at ${\sim}500^{\circ}\mathrm{C}$ and ${\sim}1000^{\circ}\mathrm{C}$. The ${^{36}\mathrm{Ar}}/{^{37}\mathrm{Ar}}/{^{38}\mathrm{Ar}}$ ratios indicate that terrestrial Ar is released only in the first extraction (Nakhla is a fall), and thus most of this ³⁸Ar_{Cl} is martian. Calculated total martian Cl is 268 ppm, of which 131 ppm released at higher temperature was certainly incorportated into the rock at formation, whereas 137 ppm released at lower temperature may represent Cl introduced by martian weathering. Some nakhlites, including Nakhla, are known to contain significant martian weathering phases (7), and even higher Cl reported for Nakhla (Table 1) probably represent martian weathering.

Table 1 presents Cl abundance calculations for WR and mineral separates of several nakhlites and shergottites, as well as Chassigny. The second column (total-Cl) is the total calculated Cl derived from ³⁸Ar_{Cl}, the third column (Mars-Cl) subtracts out low-temperature Cl that is likely grain surface contamination, and the last column (% ³⁸Ar) is the percent of the total ³⁸Ar that arises from neutron capture on Cl. For most samples, these last values are >80%, and cosmogenic and trapped ³⁸Ar are relatively minor. Argon isotopic ratios for most samples show complex variability with extraction temperature, and our martian Cl values may contain some secondary martian Cl introduced by weathering.

The primary observation to be made from Table 1 is that martian meteorites contain much lower Cl that that measured in martian surface rocks and give further confirmation that Cl in these surface rocks was introduced by brines and weathering. A secondary observation is that nakhlites tend to show higher Cl than shergottites. However, this difference may, in part, be produced by greater abundance of martian weathering product in nakhlites compared to shergottites. Except for probable Cl contamination in the first few extractions, WR and Plag samples of nakhlites MIL03346 and Y-000593 each released their ³⁸Arcl in a single broad peak at mid-to high-

temperatures, and primary (igneous) Cl cannot be separated from secondary (retentive weathering) phases, if any is present. Much of the primary Cl in martian meteorites probably resides in phosphate minerals. This is consistent in Fig. 1 with 38Ar_{Cl} degassing at lower temperatures than 38Arcos, which primarily resides in feldspar. During mineral separation according to magnetic properties, phosphate accompanies the feldspar, which probably explains higher Cl in most Plag separates compared to WR and pyroxene. As feldspar rarely exceeds ~30% abundance in shergottites, Cl in Plag separates probably is considerably higher than in WR. An exception is Los Angeles, where Cl in Plag is lower Data in Table 1 suggest that Cl than in WR. abundances in shergottites are typically <100 ppm, consistent with earlier literature data on three shergottites (Table 1).

It has been argued that Cl is twice as effective as water in lowering the melting point and promoting melting at shallower martian depths, and that significant Cl in the shergottite source region would negate any need for significant water (11). However, this conclusion was based on experiments that utilized Cl concentrations more analogous to martian surface rocks than to shergottite meteorites, and may not be applicable to shergottites. Lower Cl concentrations for shergottites are generally consistent with their K contents and an estimated K/Cl ratio for Mars of ~7 (5).



1) Rieder et al. 2004 Science 306, 1746; 2) Haskin et al. 2005 Nature 436, 66; 3) Taylor and Boynton, LPSC 40th. 2009. #1411; 4) Rao et al. 2009. EPSL doi:10.1016; 5) Dreibus & Wänke 1985 Meteoritics 20, 367; 6) Dreibus & Wänke 1999. MaPS 34, A33; 7) Bridges et al. 2000 EPSL 176, 267; 8) Park et al. 2009. GCA 73, 2177; 9)

Bogard et al. 2009. MaPS 44, 905; 10) Garrison et al. 2000. MaPS 35, 419; 11) Filiberto and Treiman 2009. Chemical Geology 263, 60; 12) Dreibus et al. 2006. LPSC 37, #1180; 13) Anand et al. 2006. MaPS 41, A16.

| Sample Te | otal-Cl | Mars-Cl | % ³⁸ Ar |
|--------------------------|-----------|----------------|--------------------|
| Nakhla WR | 286 | 268 | 96 |
| MIL03346 WR | 225 | 210 | 98.5 |
| MIL03346 Px | 29 | 26 | 65 |
| MIL03346 Plag | 847 | 753 | 34 |
| Y-000593 WR | 95 | 87 | 92 |
| Y-000593 Px | 12 | 11 | 42 |
| Y-000593 Plag | 1336 | 1320 | 99.6 |
| NWA 998 Plag | 210 | 180 | 96.4 |
| Chassigny WR | 39 | 38 | 93 |
| Zagami FG-Plag | 85 | 84 | 96 |
| Zagami FG-cPx | 24 | 24 | 84 |
| Zagami FG-Px | 27 | 27 | 88 |
| Zagami CG-Plag | 48 | 48 | 76 |
| Zagami CG-Px | 30 | 29 | 87 |
| NWA2975 Plag | 34 | 26 | 92 |
| NWA 1460 Plag | 131 | 126 | 98 |
| NWA 3171 Plag | 91 | 71 | 96 |
| NWA 3171 Glass | 54 | 43 | 92 |
| Dho 378 Plag | 30 | 23 | 84 |
| NWA 1068 WR | 16 | 13 | 89 |
| Los Angeles WR | | 131 | 98 |
| Los Angeles Px | 5.2 | 3 | 52 |
| Los Angeles Plag | | 5.7 | 66 |
| Dag 476 Plag | 26 | 12 | 90 |
| Dag 476 Px-dk | 17 | 12 | 82 |
| Dag 476 Px-lt | 18 | 13 | 92 |
| <u>Literature Data</u> : | | | <u>References</u> |
| Shergotty | | 108 | 5,6,12,13 |
| EET79001-A | | 26 | |
| EET79001-B | | 48 | |
| ALH77005 | | 14 | |
| Lafayette | | 100 | |
| | 876, 114. | | |
| NWA 998 | | 88 | |
| Y-000593 | | 101 | |
| Y-000749 | w= | 73 | |
| MIL03346 | 24 | <i>48, 156</i> | |